

# Probing the nonlocal approximation to resonant collisions of electrons with diatomic molecules

Karel Houfek\*

*Institute of Theoretical Physics, Faculty of Mathematics and Physics,  
Charles University Prague, V Holešovičkách 2, 180 00 Praha 8, Czech Republic*

T. N. Rescigno<sup>†</sup>

*Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

C. W. McCurdy<sup>‡</sup>

*Department of Applied Science and Department of Chemistry, University of California, Davis, CA 95616 and  
Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

(Dated:)

A numerically solvable two-dimensional model introduced by the authors [Phys. Rev. A **73**, 032721 (2006)] is used to investigate the validity of the nonlocal approximation to the dynamics of resonant collisions of electrons with diatomic molecules. The nonlocal approximation to this model is derived in detail, all underlying assumptions are specified and explicit expressions for the resonant and non-resonant (background)  $T$  matrix for the studied processes are given. Different choices of the so-called discrete state, which fully determines the nonlocal approximation, are discussed and it is shown that a *physical* choice of this state can in general give poorer results than other choices that minimize the non-adiabatic effects and/or the background terms of the  $T$  matrix. The background contributions to the cross sections, which are usually not considered in the resonant theory of electron-molecule collisions, can be significant not only for elastic scattering but also for the inelastic process of vibrational excitation.

PACS numbers: 34.80.-i, 34.80.Ht, 34.80.Gs

## I. INTRODUCTION

In a previous paper [1] (referred to hereafter as I) we introduced a simple two-dimensional model of electron collisions with diatomic molecules which enabled us to study the dynamics of inelastic resonant processes such as vibrational excitation

$$e^- + AB(v_i) \rightarrow e^- + AB(v_f), \quad (1)$$

and dissociative electron attachment

$$e^- + AB(v_i) \rightarrow A + B^-. \quad (2)$$

The advantage of this model with one electronic and one nuclear degree of freedom is that we can solve it exactly, without the Born-Oppenheimer approximation, using appropriate numerical techniques developed recently by Rescigno and McCurdy [2, 3]. Therefore, within our model we are able to obtain the essentially exact cross sections of the studied processes (1) and (2). Accordingly we can use this model to compare various approximate methods which have been employed to calculate the cross sections for resonant electron-molecule collisions, in particular the often used local complex potential (LCP)

approximation [4, 5] and the more sophisticated nonlocal, complex and energy-dependent potential approximation (we refer to this approximation as the *nonlocal approximation* for brevity) on which the nonlocal resonance model of Domcke *et al* is based (see [6] and references therein).

In I we defined a model Hamiltonian and constructed  $N_2$ -like and  $NO$ -like models embracing all essential features of the corresponding real electron-molecule systems. As expected, the LCP approximation, defined from the exact energy of the pole of the  $S$  matrix for the fixed-nuclei electron scattering, yielded satisfactory results for energies sufficiently above threshold but failed to reproduce the energy dependence of the cross sections near threshold.

In this paper we focus on the detailed study of the nonlocal approximation based on the Feshbach projection-operator formalism [6] and its comparison with the exact results of the two-dimensional model calculations. For that purpose, we give a thorough derivation of the nonlocal approximation to the two-dimensional model in Sec. III and write an explicit decomposition of the  $T$ -matrix for vibrational excitation into *background* and *resonant* terms. It will be shown that the background terms, which were usually considered only for elastic scattering, can play an important role even for the inelastic vibrational excitation process.

The nonlocal approximation is completely determined by the so-called discrete state (we assume only one isolated resonance in our work). Once this state is given for

---

\*houfek@mbbox.troja.mff.cuni.cz

<sup>†</sup>tnrescigno@lbl.gov

<sup>‡</sup>cwmccurdy@lbl.gov

all internuclear distances, other quantities appearing in the nonlocal approximation can be at least in principle calculated. The same numerical techniques that we used for solving the two-dimensional problem can be efficiently applied to solve the nonlocal approximation equations (see Section IV for details) and thus we are able to obtain reliable results for any given discrete state. Several alternative definitions of the discrete state can be found in the literature (see for example [7–11]) including the unique definition of Lippmann and O'Malley [12] based on the physical significance of this state. But implementation of these definitions is elaborate and it is not the purpose of this paper to decide which of these definitions gives the best nonlocal approximation. Instead, we decided to investigate the nonlocal approximation by choosing several different discrete states which vary with the internuclear distance in a well-defined way and it will be shown in Section VI that the *physical* choice of the discrete state as a square-integrable function which approximates the electronic wave function calculated at the resonant energy does not in general give better results than the other, quite arbitrary choices of the discrete state. On the contrary, we will provide evidence that the smoothness of the discrete state and of the orthogonal electronic continuum states is essential to obtain quantitatively correct results within the nonlocal approximation but only if the contributions of background terms are properly included.

## II. SUMMARY OF THE TWO-DIMENSIONAL MODEL

The detailed description of our two-dimensional model was given in I. Here we briefly summarize basic equations to define quantities needed for a discussion of the nonlocal resonance theory. We should note that the normalization of continuum states used here is different from that used in I to be consistent with the energy-normalization chosen in other papers dealing with the nonlocal theory.

We denote the unperturbed energy-normalized electronic continuum states by

$$\mathcal{J}_k^l(r) = \sqrt{\frac{2k}{\pi}} r j_l(kr) \quad (3)$$

where  $k$  denotes the electron momentum,  $l$  the electron angular momentum and  $j_l$  is the spherical Bessel function of the first kind [13] (in I the continuum states were chosen to be  $r j_l(kr)$ ). We consider molecular angular momenta to be zero thus the unperturbed energy-normalized molecular-anion continuum state is simply

$$\mathcal{E}_K(R) = \sqrt{\frac{2\mu}{\pi K}} \sin(KR) \quad (4)$$

where  $K$  is the relative momentum of A and B<sup>-</sup> in the dissociative attachment channel and  $\mu$  denotes the reduced mass of the molecule AB. In accord with the

energy-normalization the definition of the cross sections must be also changed (see below).

The full Hamiltonian of our model of the system e<sup>-</sup> + AB is

$$H = H_0 + V_{\text{int}}(R, r), \quad (5)$$

$$H_0 = T_R + V_0(R) + T_r + \frac{l(l+1)}{2r^2} \quad (6)$$

where

$$T_R = -\frac{1}{2\mu} \frac{d^2}{dR^2}, \quad T_r = -\frac{1}{2} \frac{d^2}{dr^2} \quad (7)$$

are kinetic energy operators and  $R$  and  $r$  denote molecular and electronic coordinate, respectively.

The exact wave function describing the model system at a given energy  $E = E_{v_i} + E_i$  can be written as

$$|\Psi^+\rangle = |\chi_{v_i} \mathcal{J}_{k_i}^l\rangle + \frac{1}{E - H + i\eta} V_{\text{int}} |\chi_{v_i} \mathcal{J}_{k_i}^l\rangle \quad (8)$$

where  $\chi_{v_i}(R)$  is an initial vibrational state of the neutral molecule (an eigenfunction of  $T_R + V_0(R)$ ) and  $\mathcal{J}_{k_i}^l$  describes an incoming electron with momentum  $k_i$ . The wave function  $\Psi_E^+(R, r)$  given by Eq. (8) is obviously an eigenfunction of the full Hamiltonian  $H$  with energy  $E$ .

The  $T$ -matrices for vibrational excitation and dissociative attachment are given by

$$T_{v_i \rightarrow v_f}^{\text{VE}}(E) = \langle \chi_{v_f} \mathcal{J}_{k_f}^l | V_{\text{int}} | \Psi^+ \rangle, \quad (9)$$

$$T_{v_i}^{\text{DA}}(E) = \langle \mathcal{E}_{K_{\text{DA}}} \phi_b | V_0 + V_{\text{int}} - V_b | \Psi^+ \rangle \quad (10)$$

where  $\chi_{v_f}$  and  $\mathcal{J}_{k_f}^l(r)$  are final vibrational and electronic states, respectively.  $\mathcal{E}_{K_{\text{DA}}}(R)$  describes the relative motion of the nuclei with the momentum  $K_{\text{DA}}$  and  $\phi_b(r)$  is a bound state of the electron, both in the dissociative attachment channel. We assume there is only one electronic bound state,  $\phi_b(r)$ , satisfying the equation

$$\left( T_r + \frac{l(l+1)}{2r^2} + V_b(r) \right) \phi_b(r) = -E_a \phi_b(r) \quad (11)$$

where  $V_b(r)$  is given as the limit of the interaction potential for very large internuclear distances

$$V_b(r) = \lim_{R \rightarrow \infty} V_{\text{int}}(R, r) \quad (12)$$

and  $E_a$  is the electron affinity of the “atom” B.

Finally we give the formulae for the cross sections

$$\sigma_{v_i \rightarrow v_f}^{\text{VE}}(E) = \frac{4\pi^3}{k_i^2} |T_{v_i \rightarrow v_f}^{\text{VE}}(E)|^2, \quad (13)$$

$$\sigma_{v_i}^{\text{DA}}(E) = \frac{4\pi^3}{k_i^2} |T_{v_i}^{\text{DA}}(E)|^2 \quad (14)$$

with coefficients corresponding to the choice of energy-normalized continuum states.

### III. THEORY OF THE NONLOCAL APPROXIMATION

The basic assumption leading to the nonlocal resonance theory of electron-molecule collisions [6] is the formation of a metastable molecular anion  $(AB)^-$  during the collision, i.e. the electron is captured by the molecule into a quasi-bound (resonant) state which can be approximately described by a normalized square-integrable wave function. The derivation of the nonlocal resonance theory is then based on the Feshbach projection-operator formalism [14, 15] with operators chosen to project on the *resonant* and *non-resonant* parts of the electronic Hilbert space.

Here, we will proceed in three steps. First we define projection operators  $Q$  and  $P$  playing a central role in the Feshbach theory of resonance processes. Then we will decompose the scattering  $T$ -matrix into the resonant and background (non-resonant) terms and give explicit formulas for them. Finally we will derive the effective one-dimensional Schrödinger equation describing the nuclear dynamics of the resonance state  $(AB)^-$  in a nonlocal, complex and energy-dependent potential. The solution of this basic equation of the nonlocal resonance theory contains all information needed for calculation of resonance contributions to the vibrational excitation and dissociative attachment cross sections within the Born-Oppenheimer approximation.

#### A. Projection operators $Q$ and $P$

The operator  $Q$  projecting on the resonant part  $\mathcal{Q}$  of the electronic Hilbert space  $\mathcal{H}_{\text{el}}$  is given by

$$Q = |\phi_d\rangle\langle\phi_d| \quad (15)$$

where  $\phi_d(r; R)$  is a normalized, square-integrable, and in general complex wave function approximately describing the electron in a resonant state after being captured by the molecule. To simplify our derivation we assume that there is a single isolated electronic resonance state becoming a bound state for large internuclear distances, which is true for all our models.

The projector  $P$  on the complementary (non-resonant or background) part,  $\mathcal{P}$ , of  $\mathcal{H}_{\text{el}}$  is simply

$$P = 1 - Q. \quad (16)$$

Let us now define energy-normalized electronic states  $\phi_k^+(r; R)$  as the eigenstates of the electronic Hamiltonian

$$H_{\text{el}} = T_r + \frac{l(l+1)}{2r^2} + V_{\text{int}}(R, r) \quad (17)$$

restricted on the  $\mathcal{P}$  space, i.e.

$$PH_{\text{el}}P|\phi_k^+\rangle = \frac{k^2}{2}|\phi_k^+\rangle, \quad (18)$$

where a boundary condition for  $\phi_k^+$  is determined by the incoming wave  $\mathcal{J}_k^l(r)$ . In terms of the states  $\phi_k^+$  which are usually called *background* scattering states the projector  $P$  can be expressed in the form

$$P = \int |\phi_k^+\rangle\langle\phi_k^+| k dk. \quad (19)$$

In a similar way we define electronic states  $\phi_k^-(r; R)$  but with a different boundary condition in which  $\mathcal{J}_k^l(r)$  stands for an outgoing wavefunction. The  $P$  operator expressed in these states has the same form as in Eq. (19). It should be noted here that even if  $\phi_d(r; R)$  is chosen to be independent of  $R$  the background states  $\phi_k^\pm(r; R)$  are always parametrically dependent on  $R$  because of explicit  $R$ -dependence of the operator  $H_{\text{el}}$ .

Before proceeding further we denote the matrix elements of  $V_0 + H_{\text{el}}$  in the basis  $\{\phi_d, \phi_k^+\}$  as

$$V_d(R) = V_0(R) + \langle\phi_d|H_{\text{el}}|\phi_d\rangle, \quad (20)$$

$$V_{dk}^+(R) = \langle\phi_d|H_{\text{el}}|\phi_k^+\rangle, \quad (21)$$

$$\begin{aligned} V_{kk'}^+(R) &= \langle\phi_k^+|V_0(R) + H_{\text{el}}|\phi_{k'}^+\rangle \\ &= (V_0(R) + k^2/2)\delta(k^2/2 - k'^2/2) \end{aligned} \quad (22)$$

where the last equality follows from Eq. (18) and energy-normalization of the continuum states. It is important to realize that  $V_{kk'}^+$  is diagonal only because of the appropriate choice of  $\phi_k^+(r)$ . It will be shown later that this choice is necessary to get the effective one-dimensional equation describing the nuclear dynamics in a nonlocal potential. In addition to the matrix element  $V_{dk}^+(R)$  we will need a matrix element

$$V_{dk}^-(R) = \langle\phi_d|H_{\text{el}}|\phi_k^-\rangle \quad (23)$$

to define the background and resonant  $T$  matrix for vibrational excitation.

#### B. Background and resonant $T$ -matrices for vibrational excitation

We begin by writing the full Hamiltonian given by Eq. (5) in the form

$$H = H_0 + V_1 + V_2 \quad (24)$$

where  $H_0$  is given by Eq. (6) and

$$\begin{aligned} V_1 &= PH_{\text{el}}P - T_r - \frac{l(l+1)}{2r^2} \\ &= PH_{\text{el}}P - H_{\text{el}} + V_{\text{int}}, \end{aligned} \quad (25)$$

$$V_2 = H_{\text{el}} - PH_{\text{el}}P. \quad (26)$$

The motivation for the choice of  $V_1$  is to express the  $T$ -matrix (more precisely only its *resonant* part) in terms of  $|\chi_v\phi_k^+\rangle$  instead of the unperturbed initial or final state

$|\chi_v \mathcal{J}_k^l\rangle$ . We can easily see that the state  $|\chi_{v_i} \phi_{k_i}^+\rangle$  is an eigenfunction of

$$H_0 + V_1 = T_R + V_0 + PH_{\text{el}}P \quad (27)$$

within the Born-Oppenheimer approximation which will be defined explicitly later (see Eq. (48) below).

By employing the two-potential formula for the scattering  $T$ -matrix (see [16], p. 202) we get

$$T_{v_i \rightarrow v_f}^{\text{VE}} = \langle \chi_{v_f} \phi_{k_f}^- | V_1 | \chi_{v_i} \mathcal{J}_{k_i}^l \rangle + \langle \chi_{v_f} \phi_{k_f}^- | V_2 | \Psi^+ \rangle \quad (28)$$

where  $\Psi^+(R, r)$  is given by Eq. (8), or equivalently, apart from the Born-Oppenheimer approximation used for the perturbed initial state, by

$$|\Psi^+\rangle = |\chi_{v_i} \phi_{k_i}^+\rangle + \frac{1}{E - H + i\eta} V_2 |\chi_{v_i} \phi_{k_i}^+\rangle. \quad (29)$$

The last equation shows that we can take  $\chi_{v_i}(R)\phi_{k_i}^+(r; R)$  as the initial state of the system to determine the wave function  $\Psi^+(R, r)$  which we will use later to derive the effective equation for the nuclear dynamics.

The second term of Eq. (28) corresponds to the resonant part of the  $T$ -matrix as defined in [6] and is fully determined by the resonant part  $Q\Psi^+$  of the full wave function defined below in Eq. (40). Using Eqs. (16), (21), (26) and the orthogonality  $\langle \phi_{k_i}^- | \phi_d \rangle = 0$  we obtain

$$\begin{aligned} T_{v_i \rightarrow v_f}^{\text{res}} &= \langle \chi_{v_f} \phi_{k_f}^- | H_{\text{el}} - PH_{\text{el}}P | \Psi^+ \rangle \\ &= \langle \chi_{v_f} \phi_{k_f}^- | PH_{\text{el}}Q | \Psi^+ \rangle. \end{aligned} \quad (30)$$

This expression can be further simplified if we define  $\Psi_d^+(R) = \langle \phi_d | \Psi^+ \rangle_r$  where  $\langle \dots \rangle_r$  means an integration over the electronic coordinate  $r$  only. In terms of the resonant nuclear wavefunction  $\Psi_d^+$ , for which we will derive the effective Schrödinger equation in the following subsection, the resonant part of the  $T$ -matrix can be written as

$$T_{v_i \rightarrow v_f}^{\text{res}} = \langle \chi_{v_f} | V_{dk_f}^{-*} | \Psi_d^+ \rangle. \quad (31)$$

Note that this expression differs slightly from the result of Domcke (ref. [6], Eq. (4.14)) where the matrix  $V_{dk}$  without a superscript, which corresponds to the matrix element  $V_{dk}^+$  defined by Eq. (21), was, in our opinion, used incorrectly. This small difference becomes important when the background terms defined below are added to the resonant  $T$  matrix (which was not usually the case in previous studies of resonant electron-molecule collisions), since the coupling matrix elements  $V_{dk}^\pm$  are in general complex even when the discrete state is real. The reason why we cannot use  $V_{dk}^+$  instead of  $V_{dk}^-$  is that in general, in spite of the fact that  $\phi_{k_i}^-$  belongs to  $\mathcal{P}$  space,

$$\langle \phi_{k_f}^- | \phi_k^+ \rangle \neq \delta(k_f^2/2 - k^2/2) \quad (32)$$

and therefore

$$\langle \phi_{k_f}^- | PH_{\text{el}}Q | \phi_d \rangle \neq \langle \phi_{k_f}^+ | H_{\text{el}} | \phi_d \rangle. \quad (33)$$

Instead, if we consider a special case of the *real* discrete state and if we realize that for the radial case with a real discrete state

$$\phi_k^-(r) = (\phi_k^+(r))^*, \quad (34)$$

we can simplify the matrix element between electronic wave functions in (30) as

$$\langle \phi_{k_f}^- | PH_{\text{el}}Q | \phi_d \rangle = \langle \phi_{k_f}^- | H_{\text{el}} | \phi_d \rangle = \langle \phi_d | H_{\text{el}} | \phi_{k_f}^+ \rangle = V_{dk_f}^+ \quad (35)$$

where we assumed that  $H_{\text{el}}$  is a Hermitian operator. Note that in this special case we can use the matrix element  $V_{dk}^+$  but *without complex conjugation*. In the three-dimensional case, Eq. (34) must be modified to

$$\phi_k^- = (\phi_{-\vec{k}}^+)^* \quad (36)$$

and thus  $V_{dk}^*$  in Eq. (4.14) of [6] should be replaced by  $V_{d,-\vec{k}}$  under the assumption that  $\phi_d$  is real, otherwise  $V_{dk}^{-*}$  must be used.

We now return to Eq. (28). Its first term is generally called the *background* scattering  $T$ -matrix and reads

$$\begin{aligned} T_{v_i \rightarrow v_f}^{\text{bg}} &= \langle \chi_{v_f} \phi_{k_f}^- | PH_{\text{el}}P - H_{\text{el}} + V_{\text{int}} | \chi_{v_i} \mathcal{J}_{k_i}^l \rangle \\ &= \langle \chi_{v_f} \phi_{k_f}^- | V_{\text{int}} - PH_{\text{el}}Q | \chi_{v_i} \mathcal{J}_{k_i}^l \rangle \\ &= \langle \chi_{v_f} \phi_{k_f}^- | V_{\text{int}} | \chi_{v_i} \mathcal{J}_{k_i}^l \rangle \\ &\quad - \langle \chi_{v_f} | V_{dk_f}^{-*} \mathcal{J}_{dk_i}^l | \chi_{v_i} \rangle. \end{aligned} \quad (37)$$

where

$$\mathcal{J}_{dk_i}^l(R) = \int dr \phi_d^*(r; R) \mathcal{J}_{k_i}^l(r). \quad (38)$$

is an overlap of the unperturbed incoming wave with the discrete state. These background terms are non-zero even for inelastic vibrational excitation but generally small when compared to the resonant part of the  $T$ -matrix. For an example where these terms are not negligible, see the results for the  $F_2$ -like model in Section VI below.

### C. Nuclear wave equation

To derive the basic equation of the nonlocal model which determines the effective nuclear dynamics, we begin by defining the outgoing, scattered wave part of the full wave function

$$\Psi_{\text{sc}}^+(R, r) = \Psi^+(R, r) - \chi_{v_i}(R) \phi_{k_i}^+(r). \quad (39)$$

Since  $P + Q = 1$  we can next write

$$\begin{aligned} \Psi_{\text{sc}}^+(R, r) &= Q\Psi_{\text{sc}}^+(R, r) + P\Psi_{\text{sc}}^+(R, r) \\ &= \Psi_d^+(R) \phi_d(r; R) + \int \Psi_k^+(R) \phi_k^+(r; R) dk \end{aligned} \quad (40)$$

where we have used Eqs. (15) and (19) and defined  $\Psi_k^+(R) = \langle \phi_k^+ | \Psi_{\text{sc}}^+ \rangle_r$ , the  $\mathcal{P}$  space counterpart of  $\Psi_d^+(R)$ . We next write Eq. (29) in differential form

$$(E - H) |\Psi_{\text{sc}}^+\rangle = (H_{\text{el}} - PH_{\text{el}}P) |\chi_{v_i} \phi_{k_i}^+\rangle. \quad (41)$$

By using Eq. (40) and projecting on the above equation, first with the discrete state  $\langle \phi_d |$  and then with the back-

ground scattering states  $\langle \phi_k^+ |$  we obtain a set of coupled equations

$$E\Psi_d^+(R) - T_R\Psi_d^+(R) - V_d(R)\Psi_d^+(R) - \int V_{dk}^+(R)\Psi_k^+(R)k dk = V_{dk_i}^+(R)\chi_{v_i}(R), \quad (42)$$

$$E\Psi_k^+(R) - T_R\Psi_k^+(R) - V_{dk}^+(R)^*\Psi_d^+(R) - \int V_{kk'}^+(R)\Psi_{k'}^+(R)k' dk' = 0 \quad (43)$$

where we used definitions (20)–(22) and the orthonormality of the electronic basis, and where we approximated the terms containing the nuclear kinetic energy operator,  $T_R$ , as

$$\int dr \phi_d^*(r; R) T_R \phi_d(r; R) \Psi_d^+(R) \simeq T_R \Psi_d^+(R) \quad (44)$$

$$\int dr \phi_d^*(r; R) T_R \phi_k^+(r; R) \Psi_k^+(R) \simeq 0, \quad (45)$$

$$\int dr (\phi_k^+(r; R))^* T_R \phi_d(r; R) \Psi_d^+(R) \simeq 0, \quad (46)$$

$$\int dr (\phi_k^+(r; R))^* T_R \phi_k^+(r; R) \Psi_k^+(R) \simeq T_R \Psi_k^+(R) \quad (47)$$

This approximation requires the discrete state  $\phi_d(r; R)$  and the background continuum states  $\phi_k^+(r; R)$  to depend smoothly on the internuclear distance  $R$  so that their derivatives with respect to  $R$

$$\frac{\partial \phi_d(r; R)}{\partial R} \simeq 0, \quad \frac{\partial \phi_k^+(r; R)}{\partial R} \simeq 0, \quad (48)$$

are negligible when compared to derivatives of nuclear wave functions  $\Psi_d^+(R)$  and  $\Psi_k^+(R)$ . In accord with [17] we consider these conditions to be equivalent to the statement that we employ the Born-Oppenheimer approximation in all nonlocal approximation calculations. We

should contrast this statement with the view expressed by Domcke et al. [6, 18] who claim that the nonlocal resonance theory goes beyond the Born-Oppenheimer approximation by taking into account of the nonlocality of the effective potential and thus includes some of non-Born-Oppenheimer effects.

The last term in Eq. (43) can be simplified because of the definition of  $\phi_k^+(r; R)$  in Eq. (18). By using Eq. (22) we obtain

$$\int V_{kk'}^+(R) \Psi_{k'}^+(R) k' dk' = (V_0(R) + k^2/2) \Psi_k^+(R). \quad (49)$$

Note that if we were to choose the electronic basis  $\{\phi_d, \phi_k^+\}$  completely independent of  $R$  making all non-adiabatic terms neglected in Eqs. (44)–(47) exactly zero, the continuum-continuum coupling  $V_{kk'}^+$  would be inevitably non-diagonal and difficult to deal with.

Using (49) we can formally solve Eq. (43) and write

$$\Psi_k^+(R) = \int dR' G_0^+(E, R, R') V_{dk}^+(R')^* \Psi_d^+(R') \quad (50)$$

where

$$G_0^+(E) = (E - T_R - V_0 - k^2/2 + i\eta)^{-1}. \quad (51)$$

By inserting this expression into (42) we finally get the familiar working equation of the nonlocal approximation,

$$(E - T_R - V_d(R))\Psi_d^+(R) - \int dR' F(E, R, R')\Psi_d^+(R') = V_{dk_i}^+(R)\chi_{v_i}(R) \quad (52)$$

with the nonlocal, complex and energy-dependent potential

$$F(E, R, R') = \int dR'' \int V_{dk}^+(R) G_0^+(E, R, R'') V_{dk}^+(R'')^* k dk. \quad (53)$$

Once the solution  $\Psi_d^+$  of Eq. (52) is obtained, it can be used to evaluate the *resonant* part of the  $T$ -matrix with Eq. (31) and the corresponding resonant contribution to the vibrational excitation cross section via Eq. (13). The wave function  $\Psi_d^+$  also contains all information necessary

to compute the dissociative attachment cross section using the formula

$$\sigma_{v_i}^{\text{DA}}(E) = \frac{2\pi^2}{k_i^2} \frac{K_{\text{DA}}}{\mu} \lim_{R \rightarrow \infty} |\Psi_d^+(R)|^2 \quad (54)$$



which is equivalent to Eq. (14) apart from the Born-Oppenheimer approximations made in the process of deriving of Eq. (52). There are no contributions to the dissociative attachment cross sections similar to the background terms of the  $T$  matrix in Eq. (37) for vibrational excitation within the nonlocal approximation (see Appendix for details).

#### IV. EXACT SOLUTION AND IMPLEMENTATION OF THE NONLOCAL APPROXIMATION USING EXTERIOR COMPLEX SCALING

As in I, we have made use of the exterior complex scaling (ECS) method with an implementation that combines finite-elements with the discrete-variable representation (DVR), as developed by Rescigno and McCurdy [2, 3]. We employed this method to numerically solve both the two-dimensional problem and the nonlocal nuclear wave equation (Eq. (52)). In I we provided details of how this method was implemented for the two-dimensional problem and how the cross sections can be extracted from the wave functions via surface integrals. Here we focus on how the ECS method can be used to compute the nonlocal potential of Eq. (53) and to solve Eq. (52).

The problem of evaluating the nonlocal potential in Eq. (53) is usually resolved by expansion of the Green's function (Eq. 51) into eigenstates of  $T_R + V_0(R)$  which are the molecular vibrational states  $\chi_v(R)$ . But such an expansion leads to a singular integral over electron energies which is difficult to treat unless one assumes a particular energy dependence of the discrete-state-continuum coupling  $V_{dk}^+(R)$  to be able to evaluate this singular integral analytically (see e.g. ref. [6]).

In order to perform calculations in the nonlocal approximation for an arbitrary discrete state  $\phi_d(r; R)$  and to avoid any assumptions about the energy dependence of the coupling  $V_{dk}^+(R)$  when evaluating the nonlocal potential (Eq. (53)) we have made use of the ECS method together with a DVR basis for both the electronic and nuclear degrees of freedom to discretize the  $\mathcal{P}$  space. The key step in the calculation is a scheme for evaluating the nonlocal operator  $F(E, R, R')$  of Eq. (53), which we can write as

$$F(E, R, R') = \langle \phi_d | H_{el} P \frac{1}{P(E - H_{el} - T_R - V_0 + i\eta)P} P H_{el} | \phi_d \rangle_r. \quad (55)$$

We discretize both the electronic ( $[r_i]$ ) and nuclear ( $[R_j]$ ) coordinates by introducing an exterior complex scaled DVR basis for each degree of freedom. We then solve, for each discrete value of the nuclear coordinate  $R_j$ , the electronic Born-Oppenheimer eigenvalue problem

$$\sum_k (P H_{el} P)_{i,k} \phi_n(r_k; R_j) = E_n(R_j) \phi_n(r_i; R_j). \quad (56)$$

Note that the electronic operator  $P$  is here represented as a matrix in the electronic DVR basis (with associated quadrature weights  $w_i$ ):

$$P(R_j)_{i,k} = \delta_{i,k} - Q(R_j)_{i,k} \quad (57)$$

$$Q(R_j)_{i,k} = \sqrt{w_i} \phi_d(r_i; R_j) \phi_d(r_k; R_j) \sqrt{w_k}. \quad (58)$$

We thus obtain, for each value of the nuclear coordinate  $R_j$ , a set of discretized complex energies  $E_n(R_j)$  lying in the fourth quadrant of the complex plane (see for example ref. [19], Fig. 2). Because the complex-scaled operator  $P H_{el} P$  is symmetric, but not hermitian, we have to use for the wavefunctions  $\phi_n(r; R)$  the scalar product defined without complex conjugation. The coupling elements  $V_{dn}(R_j)$  between the discrete state and the discretized continuum states can then be approximated as

$$\begin{aligned} V_{dn}(R_j) &= \int dr \phi_d(r; R_j) H_{el}(r, R_j) \phi_n(r; R_j) \\ &= \int dr \phi_n(r; R_j) H_{el}(r, R_j) \phi_d(r; R_j) \\ &\approx \sum_{i,k} \sqrt{w_i} \phi_d(r_i; R_j) H_{el}(R_j)_{i,k} \phi_n(r_k; R_j) \sqrt{w_k}, \end{aligned} \quad (59)$$

where, to simplify the discussion, we have assumed that the discrete state is real and localized in the inner region where the electronic coordinate is not complex-scaled.

Having calculated the complex electronic potential curves  $E_n(R_j)$  and coupling terms  $V_{dn}(R_j)$ , we can complete the evaluation of the nuclear Green's function by constructing

$$F(E, R_i, R_j) = \sum_n \sqrt{W_i} V_{dn}(R_i) M(n)_{i,j}^{-1} V_{dn}(R_j) \sqrt{W_j} \quad (60)$$

where the weights in Eq. (60) are those associated with the nuclear DVR basis and  $M(n)$  is the matrix representation of the operator for nuclear motion in this representation:

$$M(n)_{i,j} = (E - T_R - V_0(R) - E_n(R))_{i,j} \quad (61)$$

Note that we have avoided singularities in constructing the inverse of  $M(n)$  since the energies  $E_n(R)$  are complex whereas the total energy  $E$  of the system is always real.

Having constructed  $F(E, R_i, R_j)$ , we can then solve the nuclear wave equation (Eq. (52)) in the same nuclear DVR representation. Note that the coupling element  $V_{dk}^+(R)$  appearing on the right-hand side of Eq. (52) and in the  $T$  matrices in Eqs. (31) and (37) are at specific *real* electron energies and hence must be evaluated directly using Eq. (21) where the background continuum function  $\phi_k^+(r; R)$  is obtained by solving Eq. (18) in the electronic DVR basis under exterior complex scaling.

#### V. SPECIFIC TWO-DIMENSIONAL MODELS

In the next section, we investigate the accuracy of the nonlocal approximation and compare it with exact results

TABLE I: Parameters of the  $N_2^-$ ,  $NO^-$ , and  $F_2^-$  - like models, given in atomic units, so that the resulting potential  $V(R, r)$  is in hartrees.

Parameter	$N_2$	$NO$	$F_2$
$\mu$	12766.36	13614.16	17315.99
$l$	2 ( <i>d</i> -wave)	1 ( <i>p</i> -wave)	1 ( <i>p</i> -wave)
$D_0$	0.75102	0.2363	0.0598
$\alpha_0$	1.15350	1.5710	1.5161
$R_0$	2.01943	2.1570	2.6906
$\lambda_\infty$	6.21066	6.3670	18.8490
$\lambda_1$	1.05708	5.0000	3.2130
$R_\lambda$	-27.9833	2.0843	1.8320
$\lambda_c$	5.38022	6.0500	18.1450
$R_c$	2.40500	2.2850	2.5950
$\alpha_c$	0.40000	1.0000	3.0000

of the two-dimensional calculations. For that purpose we constructed two-dimensional models for electronic collisions with  $N_2$ ,  $NO$ , and  $F_2$  molecules. We used the same parametrization of the  $N_2$ -like and  $NO$ -like models as in I and constructed another model for the molecule  $F_2$ . Functions specifying the interaction between electronic and nuclear degrees of freedom in all models are of the form

$$V_0(R) = D_0 \left( e^{-2\alpha_0(R-R_0)} - 2e^{-\alpha_0(R-R_0)} \right), \quad (62)$$

$$V_{\text{int}}(r, R) = -\lambda(R)e^{-\alpha(R)r^2}, \quad (63)$$

$$\lambda(R) = \lambda_\infty + \frac{\lambda_0}{1 + e^{\lambda_1(R-R_\lambda)}}, \quad (64)$$

$$\lambda_0 = (\lambda_c - \lambda_\infty)(1 + e^{\lambda_1(R_c-R_\lambda)}), \quad (65)$$

$$\alpha(R) = \alpha_c \quad (66)$$

and numerical values of adjustable parameters are listed in Table I.

The resulting two-dimensional potentials,  $V(R, r)$ , and corresponding potential energy curves for the  $N_2$ -like and  $NO$ -like models can be found in the I, Figs. 2 and 3. The basic characteristics of the two-dimensional potential of the  $F_2$ -like model shown in Fig. 1 are similar to the  $N_2$  and  $NO$  models, but in this case the potential well into which the electron is captured (in the region where  $r \leq 2$ ) is much deeper at larger internuclear distances corresponding to the large electron affinity of fluorine.

In Fig. 2 we plot the potential energy curves for the  $F_2$ -like model with several vibrational states. The curve labeled  $V_0(R)$  is the potential energy of the neutral molecule and is plotted along with the local, adiabatic potential curve of the anion,  $E(R) \equiv E_{\text{res}}(R) - i\Gamma(R)/2$ , which is simply  $V_0(R)$  plus the resonance eigenvalue of  $H_{\text{el}}$  under complex scaling. The potential of the molecular anion is complex for  $R < R_c$ , and the width,  $\Gamma(R)$ , is illustrated by the shaded area around the real part  $E_{\text{res}}(R)$  of the potential. Note the asymptote of the

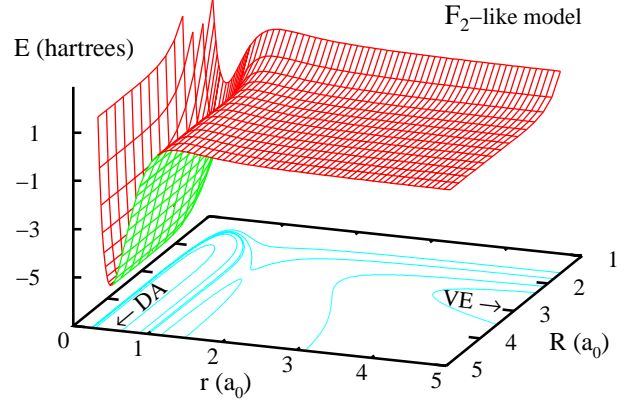


FIG. 1: (Color online) Effective two-dimensional potential  $V_0(R) + l(l+1)/2r^2 + V_{\text{int}}(R, r)$  for the  $F_2$ -like model. Internuclear distances are given in units of the Bohr radius,  $a_0 = 5.2917721 \times 10^{-11}$  m. Energies are in units of hartrees, where one hartree =  $4.359748 \times 10^{-18}$  J.

molecular anion potential energy curve lies deeply below the ground vibrational state of the neutral molecule (as in the real electron- $F_2$  system) and therefore, as we will see below, there is no threshold in the dissociative attachment cross section and no oscillatory structure in the vibrational excitation cross sections (in contrast with the  $NO$ -like model).

## VI. SENSITIVITY OF THE NONLOCAL APPROXIMATION TO CHOICE OF THE DISCRETE STATE

In Sections III and IV we have shown how to obtain the cross sections for processes (1) and (2) within the nonlocal approximation once the discrete state is given. Instead of testing various methods proposed to determine the discrete state (such as a stabilization method [8, 9], applied to electron collisions with  $H_2$  [18] and  $N_2$  [20] molecules, or a recently proposed Feshbach-Fano  $R$ -matrix method [10, 11]) we will choose several well-defined states and show what problems we can encounter if the nonlocal approximation is used to study the dynamics of electron-molecule collisions.

In general, the discrete state for large internuclear distances should become the bound state of the electron attached to one of the atoms

$$\lim_{R \rightarrow \infty} \phi_d(r; R) = \phi_b(r). \quad (67)$$

where  $\phi_b$  is defined by Eq. (11). Because the bound state is the eigenfunction of  $H_{\text{el}}$ , the discrete-state-continuum coupling  $V_{dk}(R)$  goes to zero (see Eq. (21)) as  $R \rightarrow \infty$ . If we were to choose the discrete state differently we would get a non-zero discrete-state-continuum coupling even for very large internuclear distances which has no physical

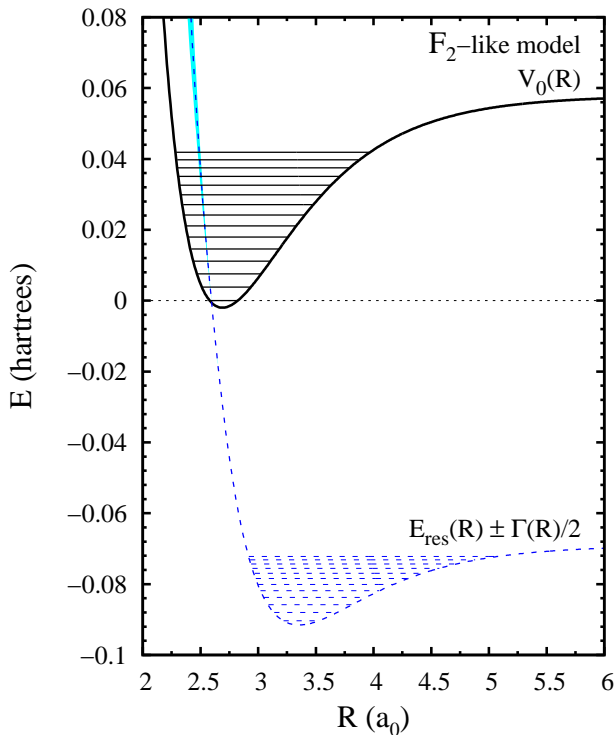


FIG. 2: (Color online) Target and anion potential energy curves for the  $F_2$ -like model with only some vibrational states plotted. Energies,  $E$ , are in units of hartrees and internuclear distances,  $R$ , are in units of  $a_0$ . Shaded area illustrates the width,  $\Gamma(R)$ , associated with the complex anion potential (see text).

meaning. Therefore we define all discrete states to satisfy the condition (67).

In the following subsections we will first show that an *intuitive* choice of the discrete state is not generally optimal because such a discrete state can change rapidly with the internuclear distance in the resonant region (to the left of the crossing point of the potential energy curves of the neutral molecule and of the molecular anion). Following that demonstration, we will choose an  $R$ -independent discrete state equal to the bound state of the electron as  $R \rightarrow \infty$ . This choice produces essentially exact results, but only if we include the background terms (Eq. (37)) in the  $T$  matrix for both elastic and inelastic electron scattering. Finally we will choose a discrete state that varies smoothly with the internuclear distance and observe that under certain circumstances the background terms can be very small and the resonant term obtained within the nonlocal approximation can be sufficient to reproduce the exact results for inelastic collisions.

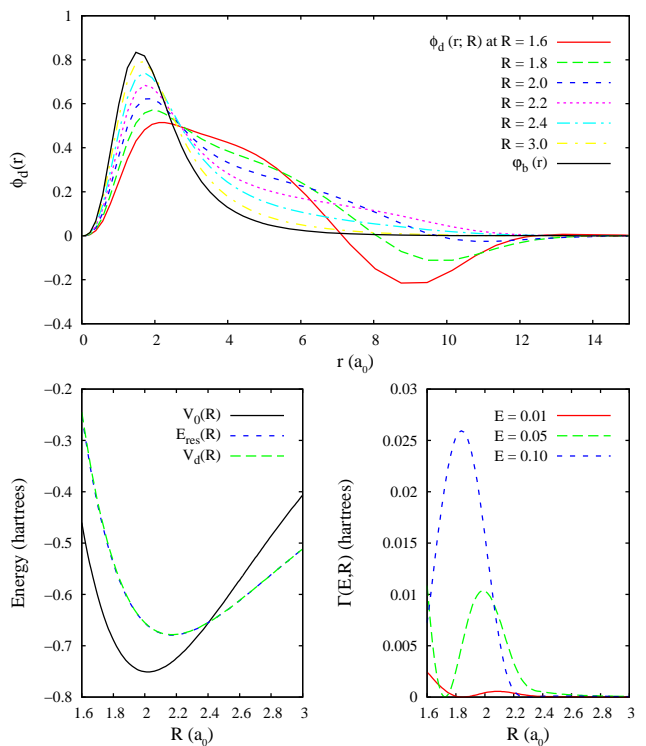


FIG. 3: (Color online)  $N_2$ -like model with the *physical* choice of the discrete state: upper panel – the discrete state at several internuclear distances; lower left panel – the potential energy curve of the neutral molecule,  $V_0(R)$  (solid line), the real part of the local complex potential of the molecular anion,  $E_{\text{res}}(R)$  (short dashed line), and the discrete state potential,  $V_d(R)$  (long dashed line), which in this case almost coincides with  $E_{\text{res}}(R)$ ; lower right panel – the  $R$ -dependence of the width defined by Eq. (68) at energies 0.01, 0.05, and 0.10 hartrees.

#### A. “Intuitive” choice of discrete state: breakdown of the Born-Oppenheimer approximation

As explained in the section III, the nonlocal approximation assumes the existence of a resonant electronic state which can be approximated by the square-integrable function, the discrete state. On the basis of this assumption one could anticipate that the best results would be obtained if the discrete state were to be chosen as a close approximation to the fixed-nuclei electron scattering wave function calculated at the resonant energy.

This resonant energy can be determined at each internuclear distance  $R$  using the exterior complex scaling method in the same way as the local complex potential was determined in I by positions of the pole of the fixed-nuclei electron scattering  $S$  matrix. When this energy is real and negative (for the internuclear distances greater than the crossing point) it is actually the energy of the electronic bound state and we can define the discrete state to be equal to this bound state. When this energy is complex, with a positive real part, i.e. we deal with a



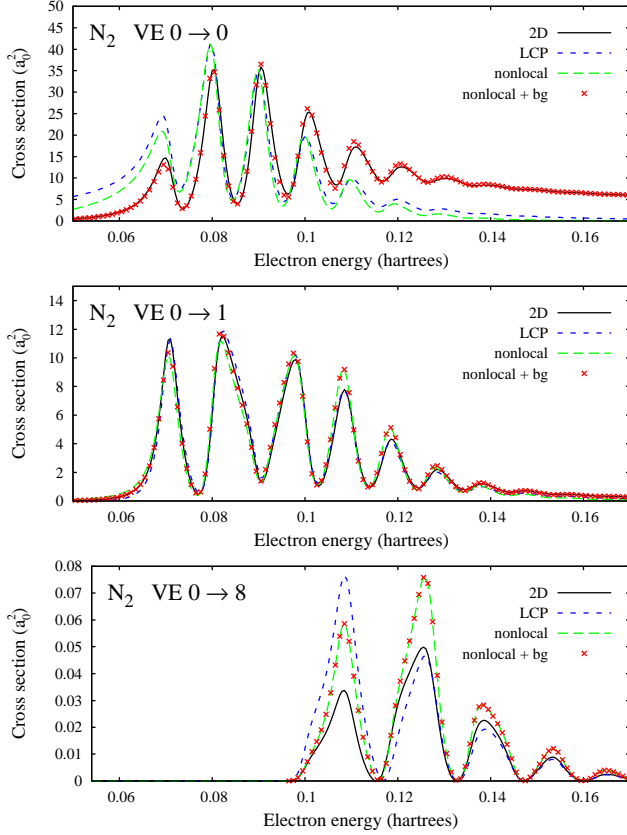


FIG. 4: (Color online) Vibrationally elastic (top panel) and inelastic ( $0 \rightarrow 1$ , middle panel, and  $0 \rightarrow 8$ , bottom panel) cross sections for the  $N_2$ -like model. The exact cross sections for our two-dimensional model (solid) are compared with cross sections obtained using the local complex potential (LCP) approximation (short dashed) and the nonlocal approximation without (long dashed) and with the background terms (crosses). The discrete state was chosen as the resonant scattering wave function cut off around  $r = 10 a_0$  (see text for details).

resonant state, we can solve the electron scattering problem at the energy equal to the real part of the complex energy and cut off *smoothly* the obtained wave function at a certain, more or less arbitrary distance  $r_d$  (the only restriction is that  $r_d$  should be sufficiently large to get a proper limit (67)). To obtain a discrete state that is smoothly varying with the internuclear distance,  $R$ , at the crossing point we multiply the discrete state defined via the scattering wave function by the appropriate factor  $\exp(-i\delta(R))$  to make it real (as the bound states are). Finally it is necessary to normalize such a discrete state to unity.

In Fig. 3, we plot the resulting discrete state for the  $N_2$ -like model for several internuclear distances (upper panel) together with the corresponding discrete-state potential  $V_d(R)$  (lower left panel) and energy-dependent resonance width defined as

$$\Gamma(E, R) = 2\pi|V_{dk}(R)|^2, \quad E = k^2/2. \quad (68)$$

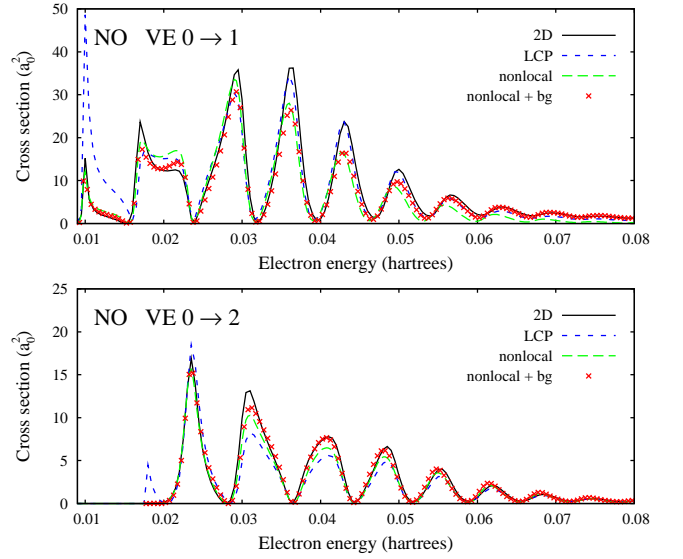


FIG. 5: (Color online) As in Fig. 4, with vibrational excitation cross sections for the NO-like model.

The cut-off function was chosen as

$$f(r) = 1 - \frac{1}{1 + e^{-(r-r_d)}} \quad (69)$$

where  $r_d = 10 a_0$ . One sees that, although the discrete-state potential  $V_d(R)$  is smooth and almost coincides with the real part of the local complex potential defined in I, the discrete state  $\phi_d(r; R)$  and the discrete-state-continuum coupling  $V_{dk}(R)$  change rapidly for small internuclear distances, suggesting that the Born-Oppenheimer approximation introduced in Eqs. (44)–(48) could break down.

The vibrational excitation cross sections from the ground state to final states  $v_f = 0, 1, 8$  for the  $N_2$ -like model are plotted in Fig. 4. In this and the following figures we compare the results of calculations obtained using the exact two-dimensional model (full curve), the local complex potential approximation investigated in I (short-dashed curve), and the nonlocal approximation without (long-dashed curve) and with (crosses) the background terms in Eq. (37). We can see that in this case the agreement between the exact and approximate results is rather good but not perfect, as one might expect for this *benchmark* system. Not surprisingly, the importance of the background scattering to the cross sections is seen to decrease with increasing inelasticity, but there is still a non-zero contribution for  $0 \rightarrow 1$  vibrational excitation. As the vibrational excitation cross section to higher vibrational states becomes smaller, discrepancies increase due to the breakdown of the Born-Oppenheimer approximation (48).

Similar results with the same definition of the discrete state were obtained for the NO- and  $F_2$ -like models, as seen in Figs. 5 and 6. In these cases the variation of the discrete state is greater than in the  $N_2$ -like model due to

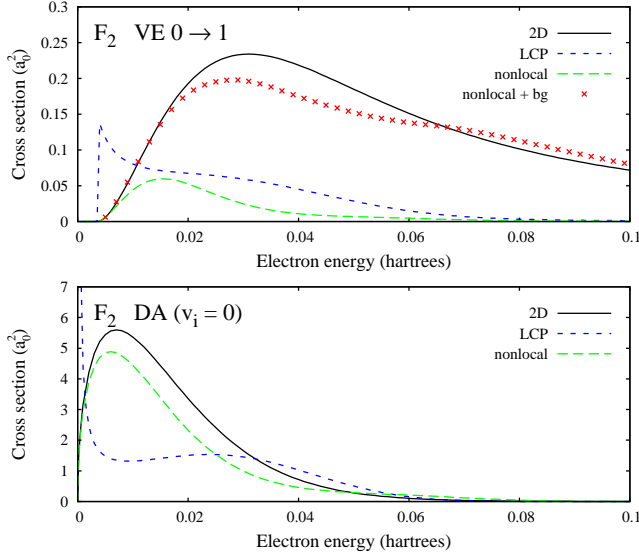


FIG. 6: (Color online) As in Fig. 4, with  $0 \rightarrow 1$  vibrational excitation (top panel) and dissociative electron detachment (bottom panel) cross sections for the  $F_2$ -like model.

the rapid increase of the resonant energy with decreasing internuclear distance. The disagreement of the non-local approximation cross sections with the exact ones is therefore even more pronounced. The disagreement of the dissociative attachment cross section calculated within the nonlocal approximation with the exact one in the lower panel of Fig. 6 demonstrates again the breakdown of the Born-Oppenheimer approximation, since as we have shown, there is no background contribution to this process in the nonlocal approximation. Note that the threshold behavior of the cross sections is correct in the nonlocal approximation due to the energy dependence of the coupling  $V_{dk}$  and nonlocal potential of Eq. (53), unlike in the local complex potential approximation where the resonance width is energy-independent (see I).

### B. Discrete state independent of internuclear distance: minimizing non-adiabatic terms and importance of background terms

In the previous subsection we have seen that an inappropriate, though intuitive choice of the discrete state can lead to the breakdown of the Born-Oppenheimer approximation. Effects of the non-adiabatic terms neglected in Eqs. (44)–(47) can be minimized if we choose the discrete state  $\phi_d(r; R)$  to be independent of the internuclear distance  $R$ . In such a case, the approximations (44) and (46) are exact and we can expect the other two to be also valid because the electronic Hamiltonian  $H_{e1}$  given by (17) is smoothly dependent on  $R$  and the continuum states  $\phi_k(r; R)$  are eigenstates of the operator  $PH_{e1}P$  where  $P$  is now independent of  $R$ .

An obvious choice of the  $R$ -independent discrete state

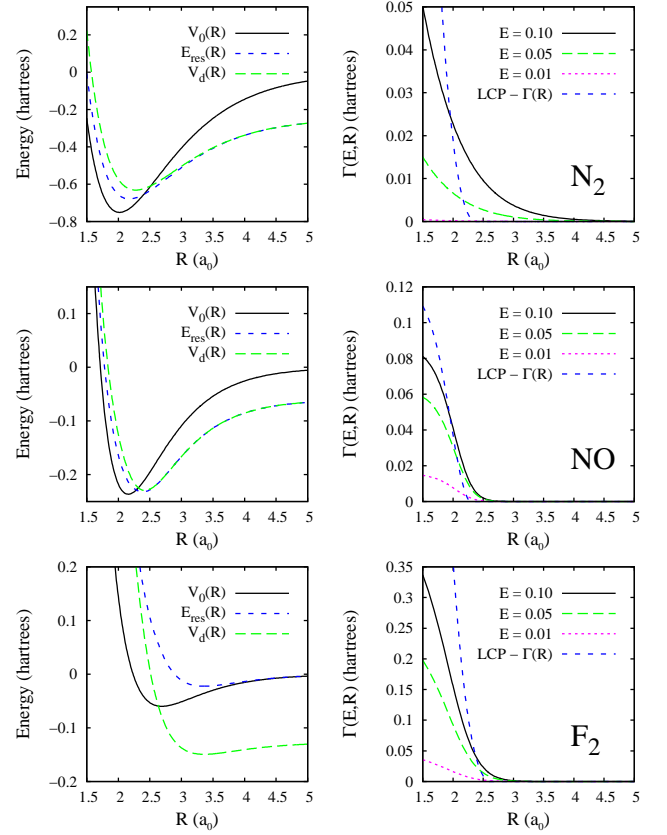


FIG. 7: (Color online) The potential energy curve of the neutral molecule,  $V_0(R)$  – solid line, the real part of the local complex potential of the molecular anion,  $E_{\text{res}}(R)$  – short dashed line, and the discrete state potential,  $V_d(R)$  – long dashed line, for the  $N_2$ -,  $NO$ -, and  $F_2$ -like model (left panels). The  $R$ -dependence of the width defined by (68) at energies 0.01, 0.05, and 0.10 hartrees and the width  $\Gamma(R)$  used in the local complex potential (LCP) approximation calculations (right panels).

is the bound state  $\phi_b(r)$  of the electron as  $R \rightarrow \infty$ , otherwise the condition of Eq. (67) would not be fulfilled. In Fig. 7 we plot the discrete-state potential  $V_d(R)$  for this particular choice together with the potential energy curves for all three models described in Section V (left panels) and the corresponding resonance widths as defined in Eq. (68) for three energies (right panels). We can see that, unlike in the previous subsection, the widths are smooth functions of the internuclear distance in all cases.

In Fig. 8 we show the cross sections for the same processes as in Figs. 4–6 (except for  $0 \rightarrow 1$  vibrational excitation in  $N_2$  where the curves are graphically indistinguishable) obtained with the  $R$ -independent discrete state. The most striking feature we can observe in this figure is that in all cases the nonlocal approximation gives essentially exact cross section if the background terms given by Eq. (37) are included. However, there are now cases where it does not suffice to consider only the resonant contribution (Eq. (31)) to the  $T$  matrix, not only

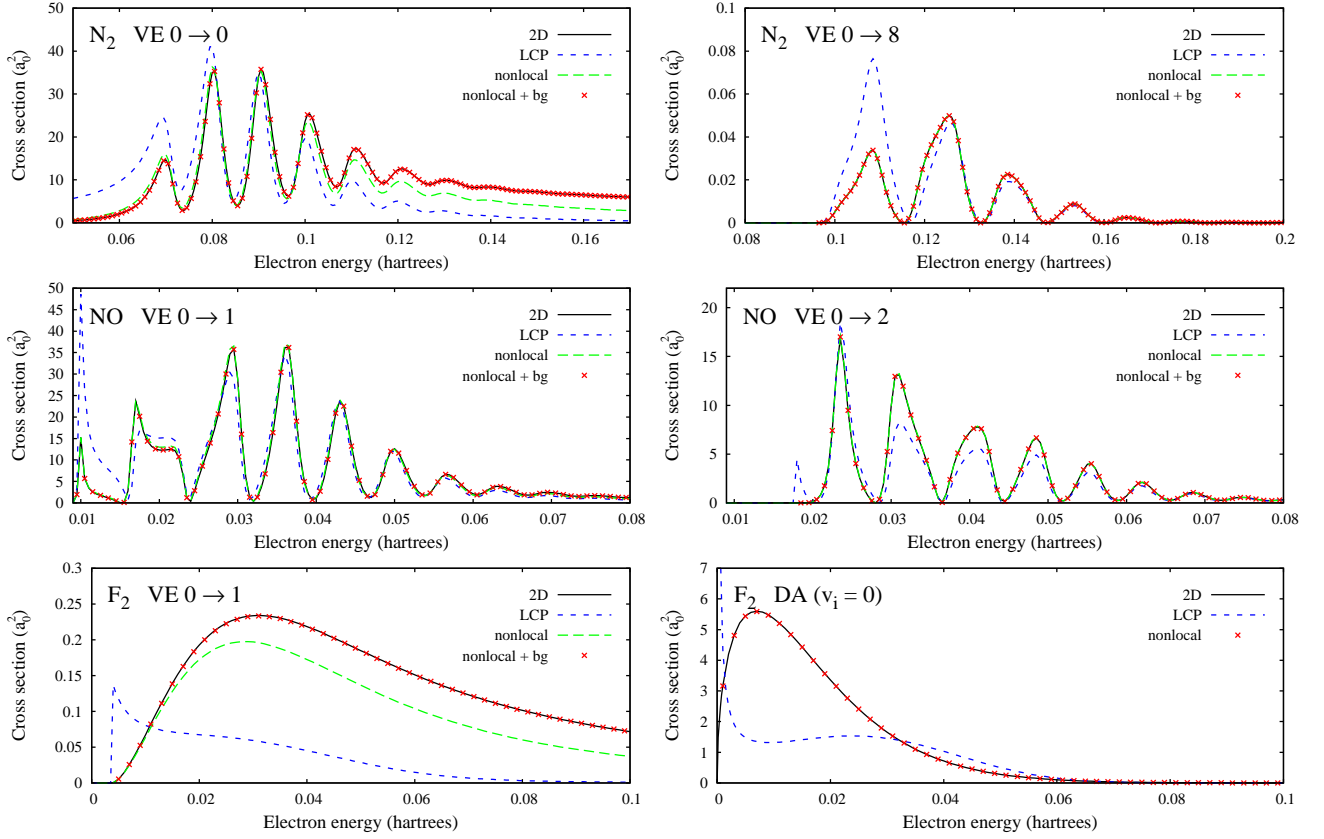


FIG. 8: (Color online) Comparison of the cross sections as in Figs. 4–6 for the discrete state chosen to be the bound state of the electron as  $R \rightarrow \infty$  for all internuclear distances, i.e. independent of  $R$ . The vibrational excitation  $0 \rightarrow 1$  cross section for the  $N_2$ -like model is omitted for results of all calculations are practically the same in this particular case.

for elastic scattering, but also for inelastic vibrational excitation (compare especially the cross sections for  $0 \rightarrow 1$  vibrational excitation in the  $F_2$ -like model).

These results can be explained if we notice the increase in the resonance width from one system to another. The largest width is found in the  $F_2$ -like model and because the background contribution to the cross section depends on this width through the coupling  $V_{dk}(R)$  in Eq. (37) one might expect that the bigger the width, the more important the background contributions.

### C. “Compact” discrete state varying smoothly with internuclear distance: decreasing background terms

In subsection VIA, we have found that the *intuitive* choice of the discrete state leads to large non-adiabatic effects and background contributions to the vibrational excitation cross sections. Later in subsection VIB we have eliminated the non-adiabatic effects by using the  $R$ -independent discrete state but the background contributions were still rather large (though smaller than in the first case) even for inelastic vibrational excitation, at least for the  $F_2$ -like model. The question is whether

it is possible to pick a discrete state which would depend smoothly on the internuclear distance  $R$  and for which the non-adiabatic effects and the background contributions to inelastic collisions would be simultaneously small.

To address this question we compare the results obtained with the nonlocal model for several well-defined discrete states. To do that in a systematic way we define  $\phi_d(r; R)$  as the lowest lying bound state of a certain electronic Hamiltonian which depends parametrically on the internuclear distance  $R$  as the Hamiltonian in Eq. (17), only the function  $\lambda(R)$  in Eq. (63) is changed in such a way that the resulting potential supports one bound state for all internuclear distances. Thus  $\phi_d(r; R)$  satisfies

$$\left( T_r + \frac{l(l+1)}{2r^2} - \lambda_d(R)e^{-\alpha_c r^2} \right) \phi_d(r; R) = E_d \phi_d(r; R). \quad (70)$$

In our calculations we used two different functions  $\lambda_d(R)$  to define  $\phi_d(r; R)$ . The first one is a slight modification of  $\lambda(R)$  defining the two-dimensional model (see Eq. (64)

$$\lambda_d(R) = \lambda_q(R) = \lambda_\infty + \frac{q \lambda_0}{1 + e^{\lambda_1(R-R_\lambda)}}, \quad (71)$$

which depends on a parameter  $q$ . Note that for  $q = 0$  we would obtain the same  $R$ -independent discrete state as

in the previous subsection since  $\lambda_d(R) = \lambda_\infty$ . For sufficiently large  $q > 0$  we would get resonant states instead of bound states for small internuclear distances and the definition of the discrete state would not be unambiguous. Therefore we take  $q \leq 0$  which will be sufficient for our discussion. The second choice of  $\lambda_d(R)$  given by

$$\lambda_d(R) = \lambda_{\text{spec}}(R) = \lambda_\infty + \frac{\lambda_{-\infty} - \lambda_\infty}{1 + e^{c_d(R-R_d)}} \quad (72)$$

is much more flexible depending on three parameters  $\lambda_{-\infty}$ ,  $c_d$ , and  $R_d$  ( $\lambda_\infty$  is given in Tab. I). Because the background contributions to the cross sections are largest for the  $F_2$ -like model we will show results only for this specific model.

In Fig. 9, top panel, we plot  $\lambda_q(R)$  for four different values of  $q$  ( $q = 0, -0.5, -1.0$ , and  $-1.5$ ), and  $\lambda_{\text{spec}}(R)$  for two different values of  $\lambda_{-\infty}$  ( $\lambda_{-\infty} = 23$  [denoted  $\lambda_{\text{spec},1}$ ] and  $\lambda_{-\infty} = 25$  [ $\lambda_{\text{spec},2}$ ], with  $c_d = 1.5$  and  $R_d = 4$ ). These functions were used to define different discrete states for the  $F_2$ -like model, shown in the bottom panel for the internuclear distance  $R = 2.5a_0$ . Corresponding discrete-state potentials  $V_d(R)$  and resonance widths  $\Gamma(E, R)$  for  $E = 0.1$  hartree are shown in the middle panels of this figure. Resonant contributions to the cross sections (see Eq. (31)) obtained using the nonlocal approximation defined by these discrete states are compared with the exact cross sections in Fig. 10. Note that we have included no background contributions in the data plotted in Fig. 10.

We observe that the resonant contribution to the cross sections can be very sensitive to the choice of the discrete state  $\phi_d(r; R)$ . Our first choice of  $\lambda_d(R) = \lambda_q(R)$  which would seem to be quite reasonable (the discrete-state potential  $V_d(R)$  follows closely the real part  $E_{\text{res}}(R)$  of the local complex potential) gives rather satisfactory results (especially for  $q$  about  $-0.5$ ) but much better agreement of the resonant contribution of the nonlocal approximation with the exact cross sections was obtained for counterintuitive choices of discrete states defined by  $\lambda_{\text{spec}}(R)$  for which the discrete-state potential  $V_d(R)$  is farther from  $E_{\text{res}}(R)$ . Notice in Fig. 9 that for  $\phi_d(r; R)$  defined by  $\lambda_{\text{spec}}(R)$  the resonance width  $\Gamma(E, R)$  is a much smoother function of  $R$  than for the other choices of  $\phi_d(r; R)$ , especially in the region around the crossing point, which can be one reason why the background contributions given by Eq. (37) are much smaller in these particular cases.

We have thus found that the less intuitive choices for the discrete state, which result in relatively larger differences between  $V_d(R)$  and  $E_{\text{res}}(R)$  at small  $R$ , and which therefore shift more information about the system into the nonlocal part of the potential  $F(E, R, R')$  rather than into  $V_d(R)$ , can give better results than the more intuitive choices. These nonintuitive choices apparently increase the resonant contribution relative to the background. In our particular model study this happens when the discrete state is rather *compact* (more localized, see Fig. 9, bottom panel) compared with the bound state of the electron as  $R \rightarrow \infty$  and with the resonant states used in subsection VIA.

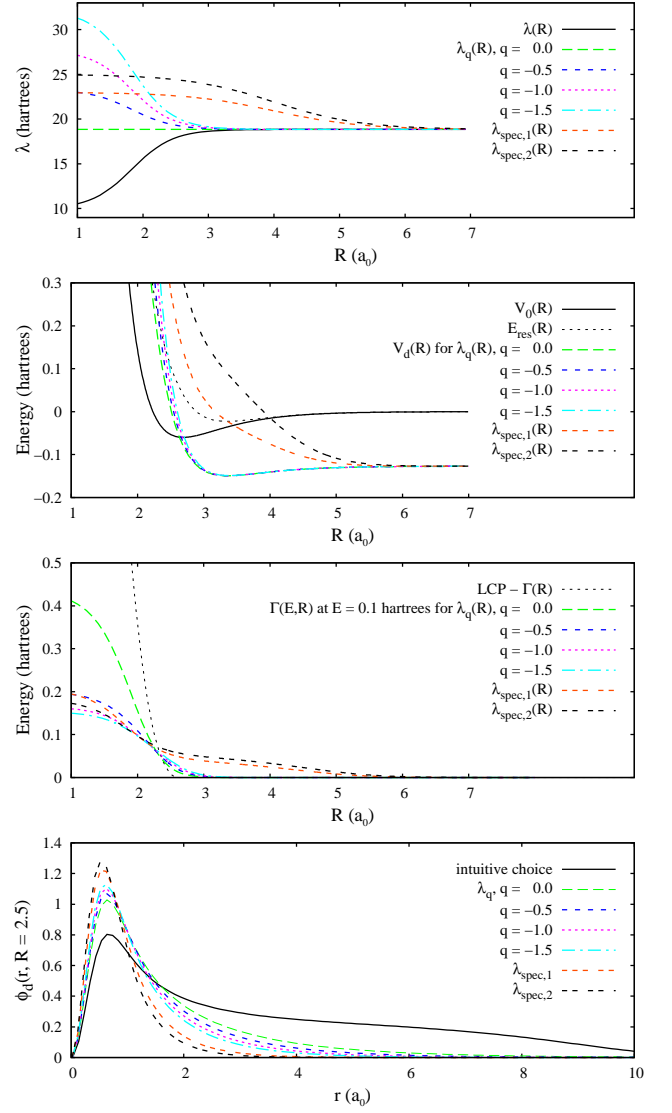


FIG. 9: (Color online) Top panel –  $\lambda(R)$ , which defines the interaction potential  $V_{\text{int}}(r, R)$ , and  $\lambda_d(R)$ , which define the discrete state  $\phi_d(r; R)$ , for the  $F_2$ -like model. Middle panels – discrete-state potentials and  $R$ -dependence of the resonance width  $\Gamma(E, R)$  for  $E = 0.1$  hartree corresponding to different discrete states defined by  $\lambda_d(R)$ . Bottom panel – discrete states at  $R = 2.5 a_0$ .

We should note that if we were to include the background contributions to the cross sections we would again get very good agreement with the exact cross sections in all cases except the one defined by  $\lambda_q(R)$  with  $q = -1.5$ , where small discrepancies due to the breakdown of the Born-Oppenheimer approximation were found (we can see this in the dissociative attachment cross section in the bottom panel of Fig. 10).

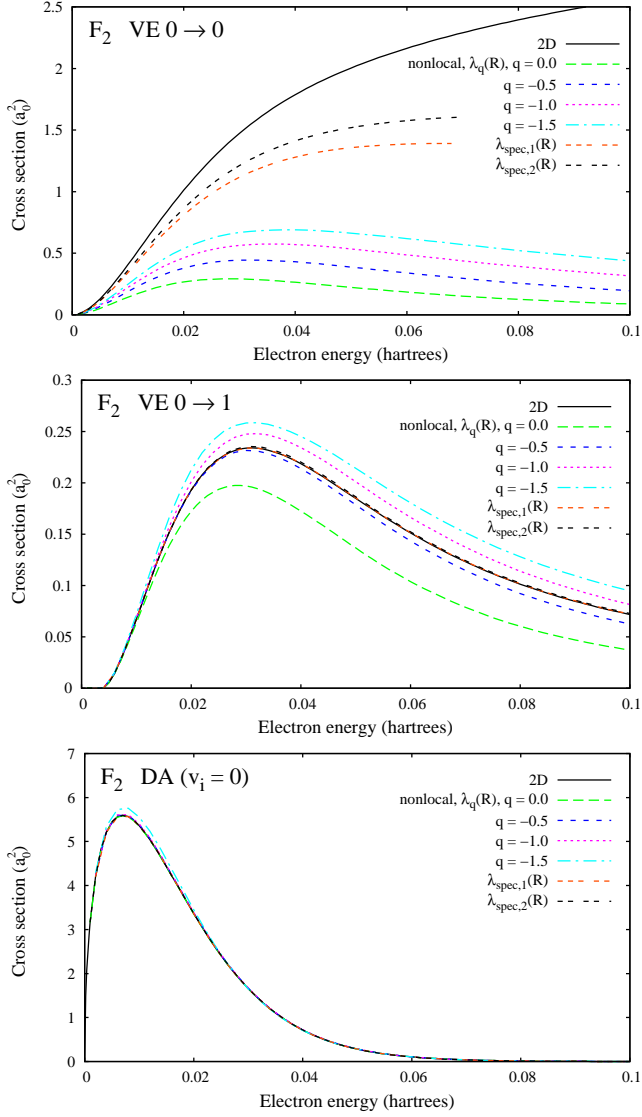


FIG. 10: (Color online) Elastic (top panel), vibrational excitation  $0 \rightarrow 1$  (middle panel), and dissociative attachment (bottom panel) cross sections for the  $F_2$ -like model. The exact cross sections of the two-dimensional model (solid) are compared with the resonant contribution (see Eq. (31)) to cross sections obtained using the nonlocal approximation with different choices of the discrete state (line types as in Fig. 9). Note that no background contributions are included in these results.

## VII. CONCLUSION

In this work we have investigated, using the 2D model introduced in I, the nonlocal approximation to the dynamics of resonant electron scattering from diatomic molecules. We have completely rederived the basic equations of the nonlocal approximation in the context of this two-dimensional model and have given explicit expressions for the background contributions to the vibrational excitation cross sections.

We have constructed three two-dimensional models similar to the real diatomic systems and used several well-defined discrete states to probe the relevance of the nonlocal approximation for the description of the studied processes. We have found that an inappropriate choice of the discrete state, though it would seem to be supported by physical assumptions of the theory of resonant processes, can lead to inaccurate results due to the breakdown of the Born-Oppenheimer approximation defined here by neglecting the terms containing derivatives of the discrete state and orthogonal scattering states with respect to the internuclear distance. On the other hand, if we pick a discrete state which varies smoothly with the internuclear distance then the cross sections obtained within the nonlocal approximation agree with the exact cross sections very well, but in general only if the background contributions to the vibrational excitation  $T$  matrix are taken into account. Although we have been able to find for our two-dimensional model particular discrete states for which the background contributions are negligible, it is not clear that this will also be the case when we deal with a real diatomic system. Therefore, we suggest that new *ab initio* methods proposed to calculate the discrete-state potential  $V_d(R)$  and the discrete-state-continuum coupling  $V_{dk}(R)$  (such as e.g. the Feshbach-Fano  $R$ -matrix procedure [10, 11]) should also consider developing tools for calculation of these background contributions to the vibrational excitation  $T$  matrix.

Because of the difficulty of incorporating the background contributions into the nonlocal resonance model [6] which does not define a discrete state explicitly but rather assumes some functional dependence for the discrete-state potential  $V_d(R)$  and for the discrete-state-continuum coupling  $V_{dk}(R)$ , the parameters of which are usually found by fitting eigenphase sums for fixed-nuclei electron scattering, we did not use this approach here. Nevertheless, it would be probably worthwhile to see whether the nonlocal approximation defined by such a method would also give negligible background contributions for all inelastic processes, as is usually assumed.

Another important question which requires further study is when the nonlocal approximation breaks down. The only approximation we made in the process of derivation of the nonlocal approximation was the Born-Oppenheimer approximation expressed by Eq. (48). It was first used for the perturbed initial and final state, Eqs. (28) and (29), and later for matrix elements of the nuclear kinetic energy operator, Eq. (44)–(47). Although one can always choose the discrete state to be slowly varying with or completely independent of the internuclear distance it is not obvious that the background scattering states will also vary slowly, especially for polar molecules such as hydrogen halides for which the dipole interaction of the electron with the molecule can change rapidly with the internuclear distance. Moreover, the reduced mass of the molecule in all our models was quite large (greater than  $10^4 m_e$ ). Therefore, further tests of the nonlocal approximation using  $H_2^-$ ,  $HF^-$ , or  $HCl^-$  -



like two-dimensional models should be carried out.

In summary, we have found that the nonlocal model gives an excellent description of the scattering process in cases where the collision is well described by electron capture into a compact, localized state. If this state varies smoothly with internuclear distance, then the conditions underlying the Born-Oppenheimer approximation, which is central to the derivation of the nonlocal model, are satisfied and the nonlocal model can work quite well, even close to threshold. In cases where the resonance width becomes large over nuclear geometries that lie within the Franck-Condon region of the initial state, then background contributions to the  $T$ -matrix for vibrational excitation can become important. The  $F_2^-$  case presents such a situation. In such cases there can be considerable sensitivity of the computed cross sections to the choice of the discrete state, reflected either in large background contributions or a breakdown of the Born-Oppenheimer approximation. This may simply be a reflection of the fact that electron scattering in cases involving broad resonances are difficult to describe with a pure resonance model.

### Appendix

Here we show explicitly that there are no *background* terms in the dissociative attachment cross section (except terms neglected due to the Born-Oppenheimer approximation) if the discrete state  $\phi_d(r; R)$  (see Eq. (15)) is chosen properly to coincide with the electronic bound state  $\phi_b(r)$  as  $R \rightarrow \infty$  (see Eq. (11)).

To derive the formula (54) for the dissociative attachment cross section within the nonlocal approximation we begin with the exact cross section (see I, Section III.B for details, noting that the coefficient  $4\pi/k_i$  was changed to  $2\pi^2/k_i^2$  due to the energy-normalization of the electronic continuum states, Eq. (3)) given by

$$\sigma_{vi}^{DA}(E) = \frac{2\pi^2}{k_i^2} \lim_{R \rightarrow \infty} \int_0^\infty \vec{F}_{DA}(R, r) \cdot \vec{n}_R dr \quad (73)$$

where  $k_i$  is momentum of an incoming electron and the flux  $\vec{F}_{DA}$  projected into the dissociative attachment channel in the direction of a unit vector  $\vec{n}_R$  for the molecular coordinate  $R$  can be written as

$$\begin{aligned} \vec{F}_{DA} \cdot \vec{n}_R = & \frac{1}{2\mu i} \left[ (P_{DA} \Psi_{sc}^+)^* \frac{\partial}{\partial R} P_{DA} \Psi_{sc}^+ \right. \\ & \left. - P_{DA} \Psi_{sc}^+ \frac{\partial}{\partial R} (P_{DA} \Psi_{sc}^+)^* \right]. \end{aligned} \quad (74)$$

The expression (73) for the cross section is equivalent to (14) where the  $T$ -matrix is given by (10).

The projector operator  $P_{DA}$  is defined as

$$P_{DA} \Psi_{sc}^+(R, r) = \phi_b(r) \int_0^\infty \phi_b^*(r') \Psi_{sc}^+(R, r') dr. \quad (75)$$

If we substitute  $\Psi_{sc}^+$  from Eq. (40) and realize that only the limit as  $R \rightarrow \infty$  is important for evaluation of the cross section we obtain

$$\lim_{R \rightarrow \infty} P_{DA} \Psi_{sc}^+(R, r) = \phi_b(r) \lim_{R \rightarrow \infty} \Psi_d^+(R) \quad (76)$$

under the assumption

$$\lim_{R \rightarrow \infty} \phi_d(r; R) = \phi_b(r). \quad (77)$$

For the projected flux (74) we finally get

$$\lim_{R \rightarrow \infty} \vec{F}_{DA} \cdot \vec{n}_R = \frac{K_{DA}}{\mu} |\phi_b(r)|^2 \lim_{R \rightarrow \infty} |\Psi_d^+(R)|^2 \quad (78)$$

where we have used

$$\lim_{R \rightarrow \infty} \frac{\partial}{\partial R} \Psi_d^+(R) = \lim_{R \rightarrow \infty} i K_{DA} \Psi_d^+(R) \quad (79)$$

which follows from the asymptotic behavior of the scattered wave function (see I, Eq. 16).

Because the electronic bound state  $\phi_b(r)$  is normalized the integration over the electronic coordinate  $r$  in Eq. (73) is trivial and we finally obtain Eq. (54) for the dissociative attachment cross section.

### Acknowledgments

This work was performed under the auspices of the US Department of Energy under contract DE-AC02-05CH11231 and was supported by the U.S. DOE Office of Basic Energy Sciences, Division of Chemical Sciences. Support from the Czech Science Foundation by Grant No. 202/07/0833 is greatly acknowledged. CWM was partially supported by the National Science Foundation (Grant No. PHY-0604628).

- 
- [1] K. Houfek, T. N. Rescigno, and C. W. McCurdy, Phys. Rev. A **73**, 032721 (2006).  
 [2] T. N. Rescigno and C. W. McCurdy, Phys. Rev. A **62**, 032706 (2000).

- [3] C. W. McCurdy, M. Baertschy, and T. N. Rescigno, J. Phys. B **37**, R137 (2004).  
 [4] D. T. Birtwistle and A. Herzenberg, J. Phys. B **4**, 53 (1971).

- [5] L. Dubé and A. Herzenberg, Phys. Rev. A **20**, 194 (1979).
- [6] W. Domcke, Phys. Rep. **208**, 97 (1991).
- [7] T. F. O'Malley, Phys. Rev. **185**, 101 (1969).
- [8] E. Holøien and J. Midtdal, J. Chem. Phys. **45**, 2209 (1966).
- [9] A. U. Hazi and H. S. Taylor, Phys. Rev. A **1**, 1109 (1970).
- [10] B. M. Nestmann, J. Phys. B **31**, 3929 (1998).
- [11] P. Kolorenč, V. Brems, and J. Horáček, Phys. Rev. A **72**, 012708 (2005).
- [12] B. A. Lippmann and T. F. O'Malley, Phys. Rev. A **2**, 2115 (1970).
- [13] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover Publications, New York, 1972).
- [14] H. Feshbach, Annals of Phys. **5**, 357 (1958).
- [15] H. Feshbach, Annals of Phys. **19**, 287 (1962).
- [16] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, New York, 1964).
- [17] T. F. O'Malley, Adv. At. Mol. Phys. **7**, 223 (1971).
- [18] M. Berman, C. Mündel, and W. Domcke, Phys. Rev. A **31**, 641 (1985).
- [19] C. W. McCurdy and F. Martín, J. Phys. B **37**, 917 (2004).
- [20] M. Berman and W. Domcke, Phys. Rev. A **29**, 2485 (1984).